

# Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/GB05/001322

International filing date: 05 April 2005 (05.04.2005)

Document type: Certified copy of priority document

Document details: Country/Office: GB  
Number: 0407804.4  
Filing date: 06 April 2004 (06.04.2004)

Date of receipt at the International Bureau: 03 October 2005 (03.10.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland  
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse



INVESTOR IN PEOPLE

The Patent Office  
Concept House  
Cardiff Road  
Newport  
South Wales  
NP10 8QQ

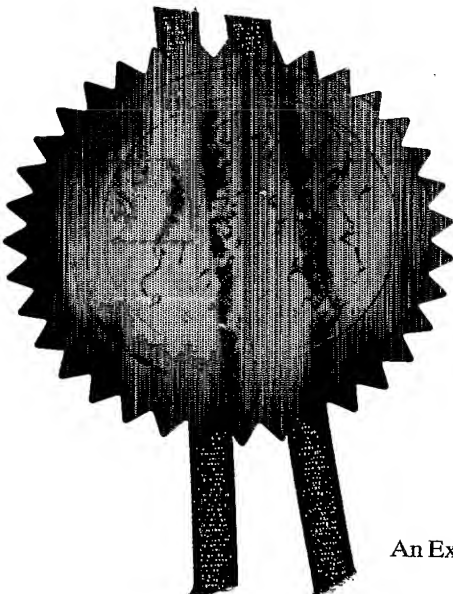
I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

I also certify that the attached copy of the request for grant of a Patent (Form 1/77) bears an amendment, effected by this office, following a request by the applicant and agreed to by the Comptroller-General.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.



Signed

*William Morell*

Dated

22 September 2005



## Patents Form 1/77

Patents Act 1977  
(Rule 16)

The  
Patent  
Office

THE PATENT OFFICE  
WIM  
06 APR 2004  
RECEIVED BY FAX

1/77

## Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form.)

The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

1. Your reference

IP/P7360

06APR04 E8B6944-1 D02776

P01/7700 0.00-0407804.4 ACCOUNT CHA

2. Patent application number

(The Patent Office will fill in this part)

0407804.4

6 APR 2004

3. Full name, address and postcode of the or of each applicant (underline all surnames)

QINETIQ LIMITED

Registered Office 85 Buckingham Gate  
London SW1E 6PD  
United Kingdom

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

GB

8307431001

4. Title of the invention

MANUFACTURE OF CADMIUM MERCURY TELLURIDE

5. Name of your agent (if you have one)

P DAVIES et al

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

QINETIQ LIMITED

IP Formalities

A4 Bldg

Cody Technology Park

Ively Road

Farnborough

Hants GU14 0LX United Kingdom

Patents ADP number (if you know it)

8183873001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or  
b) there is an inventor who is not named as an applicant, or  
c) any named applicant is a corporate body.  
See note (d))

YES (b)

Patents Form 1/77

Patents Form 1/77

0100152: 06-Apr-04 05:10

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	0
Description	19 /
Claim(s)	5 /
Abstract	1 /
Drawing(s)	4 /

10. If you are also filing any of the following, state how many against each item.

Priority documents	0
Translations of priority documents	0
Statement of inventorship and right to grant of a patent ( <i>Patents Form 7/77</i> )	1 /
Request for preliminary examination and search ( <i>Patents Form 9/77</i> )	1 /
Request for substantive examination ( <i>Patents Form 10/77</i> )	0
Any other documents ( <i>please specify</i> )	0

11. I / We request the grant of a patent on the basis of this application.

Signature

P DAVIES

P DAVIES

Date  
6.4.04

12. Name and daytime telephone number of person to contact in the United Kingdom

Linda Bruckshaw 01252 392722

**Warning**

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent of the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

**Notes**

- If you need help to fill in this form or have any questions, please contact the Patent Office on 0645 500305.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have attached 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

Patents Form 1/77

0100152 06-Apr-04 05:10

## DUPLICATE

1

## Manufacture of Cadmium Mercury Telluride

This invention relates to a method of manufacture of cadmium mercury telluride, especially to a method of forming cadmium mercury telluride layers that can be  
5 used in infrared devices and the cadmium mercury telluride structures so grown.

Cadmium mercury telluride,  $Hg_{1-x}Cd_xTe$ , is well known as a material for use in infrared devices, such as detectors, sources, LEDs, negative luminescence devices etc.. Cadmium mercury telluride, referred to as CMT (or sometimes  
10 MCT) is a semiconductor alloy, the bandgap of which can be varied by altering the composition of the alloy, i.e. the cadmium content  $x$ . The band gap may be tuned so that CMT can be used for a range of infrared devices covering short wave (SW), medium wave (MW), long wave (LW) and very long wave (VLW) infrared wavelengths. CMT is the material of choice for many infrared focal plane  
15 array applications. Low leakage current and high carrier mobility result in detectors with excellent sensitivity. CMT is the best solution for single and multi-band systems covering a wide range of wavelengths because it is possible to tune the wavelength by selecting the appropriate composition and it is possible to design and grow structures where the composition is tuned so that two or more  
20 wavelengths are operational within a single device.

The general principle for fabricating infrared devices is well established. CMT is grown epitaxially onto a crystalline substrate. Devices are then formed by Mesa etching, ion implantation or ion beam milling. Metal contacts are then formed and  
25 the devices bonded to a silicon read out circuit. Note that CMT is also grown as bulk crystals from which devices are made by ion implantation or ion beam milling but epitaxial growth can be advantageous over bulk crystal growth.

Various epitaxial growth methods have been suggested for fabricating CMT.  
30 Metal-organic vapour phase epitaxy (MOVPE) has been successfully used as a technique for reproducible and uniform growth over large areas. US patent 4,650,539 describes manufacture of CMT using MOVPE. US patent 4,566,918 is a modification of this technique which grows thin layers of CdTe and HgTe which

interdiffuse to form a uniform CMT structure. US patent 4,950,621 describes a MOVPE technique for CMT growth which uses a photocatalytic decomposition of the metal-organic compounds.

- 5 Other methods for growing CMT include molecular beam epitaxy (MBE). Infrared devices have been formed from CMT grown on a cadmium zinc telluride ( $\text{Cd}_{1-y}\text{Zn}_y\text{Te}$  also known as CZT) substrate by an MBE process. See for example; M Zandian, JD Garnett, RE Dewames, M Carmody, JG Pasko, M Farris, CA Cabelli, DE Cooper, G Hildebrandt, J Chow, J M Arias, K Vural and DNB Hall, J. Electronic Materials 32(7) 803 (2003) "Mid- wavelength infrared p-on-n  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  heterostructure detectors: 30-120 Kelvin state of the art performance", or JD Phillips, DD Edwall and a DL Lee J. Electronic Materials 31(7) 664 (2002) "Control of very long wavelength infrared  $\text{HgCdTe}$  detector cut-off wavelength".
- 10
- 15 Infrared imaging applications increasingly demand large area, two dimensional detector arrays for long range detection and identification. As the physical size of these arrays has increased so the limitations of traditional substrate materials and growth techniques for CMT have become apparent. Cadmium zinc telluride has been widely used as a substrate for CMT growth but is only available in small
- 20 sizes which limits its usefulness for the production of large arrays. Cadmium telluride, which has likewise been used as a substrate, is also only available in small sizes. Further, both  $\text{CdTe}$  and CZT are extremely fragile and the crystal quality is not particularly good.
- 25 Gallium arsenide (GaAs) substrates are available in relatively large sizes. However as mentioned the devices are usually bonded to a silicon read-out circuit. In operation detectors are often cooled to low temperatures, for example around 80K (although different devices work best at different temperatures) to reduce thermal noise. At the operating temperatures of the detectors the thermal
- 30 mismatch between the silicon read out circuit and GaAs substrate can cause delamination of the infrared devices from the circuitry. This effect can be reduced by thinning the substrate but thinning processes can be complex, reducing yields

and increasing production costs. This problem of thermal mismatch also applies to cadmium telluride and CZT substrates.

Were silicon to be used as a substrate, the substrate would inherently be  
5 thermally matched to the read out circuitry, however, to date, it has proved extremely difficult to produce arrays of working CMT devices on a silicon substrate. For example, individual working LW detector devices have been produced on silicon substrates with good performance but arrays of such devices contain few good working detectors i.e. the operability of the array is very poor.

10

Silicon has a further advantage as a substrate in that it has a high thermal conductivity. This leads to faster cool down to device operating temperatures which is especially useful for detectors. It is also beneficial for effective removal of heat from infrared sources.

15

MBE techniques have been applied to growing CMT on silicon, growing buffer layers on the silicon prior to CMT growth, for example;- T.J. de Lyon, J.E. Jensen, M.D. Gorwitz, C.A. Cockrum, S.M. Johnson and G.M. Venzor, J. Electronic Materials. 28, 705 (1999). MBE growth of CMT on silicon has proved a  
20 challenging task. Firstly, for MBE growth of CMT on any substrate the growth temperature must be accurately controlled, requiring reproducible wafer mounting techniques and fine substrate temperature control. Secondly, material defects have proved difficult to eliminate. These defects do not always have a severe effect on medium wavelength infrared device characteristics (depending on the  
25 device) but they do detrimentally affect long-wavelength devices. Consequently growth of CMT on silicon by MBE is a difficult process and has only produced acceptable mid-wavelength infrared devices and arrays.

MOVPE growth of CMT on silicon to produce working devices has also been  
30 problematic. See J Electronic Materials 25(8) (1996) page 1347 K Shigenaka, K Matsushita, L Sugiura, F Nakata and K Hirahara, M Uchikoshi, M Nagashima and H Wada "Orientation dependence of HgCdTe epitaxial layers grown by MOCVD on silicon substrates",



page 1353 K Maruyama, H Nishino, T Okamoto, S Murakami, T Saito, Y Nishijima, M Uchikoshi, M Nagahima and H Wada "Growth of (111) HgCdTe on (100) Si by MOVPE using metal organic tellurium absorption and annealing", or Page 1358 H Ebe, T Okamoto, H Nishino, T Saito and Y Nishijima, M Uchikoshi,  
5 M Nagashima and H Wada "Direct growth of CdTe on (100), (211), and (111) Si by metal organic chemical vapour deposition".

There is therefore a desire for a method of growing CMT on a variety of substrates, especially silicon. Further it is desired that reproducible, large scale  
10 growth can be achieved and that the properties of the CMT can be controlled to give wavelength specific performance. It also obviously wished that the method be part of a viable process of fabricating working infrared devices.

It is an object of the invention to provide a method of manufacture of CMT which  
15 meets at least some of these aims.

Thus according to the present invention there is provided a method of growing cadmium mercury telluride,  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  where  $0 \leq x \leq 1$ , comprising the steps of taking a crystalline substrate, growing at least one buffer layer on said substrate  
20 by molecular beam epitaxy and subsequently growing at least one layer of cadmium mercury telluride on said at least one buffer layer by metal-organic vapour phase epitaxy.

The present invention therefore is a combination of MBE and MOVPE  
25 techniques. At least one buffer layer is grown on the substrate material by MBE. CMT is then grown on top of the at least one buffer layer using an MOVPE technique. The buffer layers can prevent chemical contamination of the CMT layers by atoms in the substrate layer, for instance gallium atoms if the substrate is gallium arsenide, and can relieve lattice mismatch in the CMT layers. The  
30 MBE process allows sufficiently thick, good quality buffer layers to be grown which provide a basis for CMT growth. CMT can then be grown on the buffer layers by MOVPE in a controlled, reproducible fashion. Further the at least one buffer layer can protect the substrate during the subsequent MOVPE processing

— some substrates are generally not suitable for MOVPE processing because of chemical attack during MOVPE.

The present invention therefore combines both MBE and MOVPE to produce  
5 CMT which can be used in devices at a wide range of wavelengths with good  
qualities. This goes against the conventional thinking in the field which is to seek  
to use either an all MBE or an all MOVPE process. Whilst the method of the  
present invention does require two distinct processing steps, adding to the  
complexity of the method, the present inventors have realised that mixing the two  
10 techniques can provide a reliable and controllable process that has produced  
excellent devices.

As used in this specification the term cadmium mercury telluride means the  
composition  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  where  $x$  is controlled to lie between 1 and 0 inclusive.  
15 When  $x$  is 1 the substance is actually cadmium telluride and when  $x$  is 0 the  
material is actually mercury telluride but both shall be included within the term  
cadmium mercury telluride or CMT for the purposes of this specification.

The substrate could be any suitable crystalline material. The substrate may  
20 conveniently be physically robust and, for large area detectors, available in large  
areas. In some applications it is necessary that the substrate in the final device is  
transparent to infrared radiation of the appropriate wavelength although this can  
be achieved by thinning the substrate. Suitable substrate materials include  
cadmium telluride, zinc telluride, cadmium zinc telluride, cadmium zinc selenide  
25 and cadmium zinc selenide telluride (although these are generally not available in  
large sizes), gallium arsenide, silicon, germanium, indium antimonide, indium  
aluminium antimonide, indium gallium antimonide, indium phosphide, sapphire,  
alumina or spinel ( $\text{MgAl}_2\text{O}_4$ ).

30 Silicon is a preferred substrate in some embodiments as it is inherently thermally  
matched with the read-out circuit. The method of the present invention allows  
device structures to be grown on silicon and tuned to operate at any wavelength

across the whole range of infrared wavelengths with very good device performance.

Orientation of the substrate is important in ensuring the correct material growth.

5 The orientation should allow correct growth of the buffer layers by MBE and ensure that the buffer layers have the correct orientation for the growth of CMT by MOVPE. The substrate is therefore preferably arranged to be misaligned from the form {100} in either the  $\langle 111 \rangle$  or  $\langle 110 \rangle$  directions. Preferably the degree of misalignment is between  $1^\circ$  and  $10^\circ$ . Mis-aligning the substrate orientation in this

10 way prevents the build up of defects in the MBE buffer layers. When the substrate is silicon the substrate orientation is preferably (001) mis-aligned towards the [111] direction and the degree of mis-alignment is preferably in the range of  $1^\circ$ – $10^\circ$  inclusive. Silicon is generally a more difficult substrate to grow on and correct orientation can be important.

15 The choice of buffer layer or layers may depend on the substrate used. The buffer layers set the correct orientation for MOVPE growth and prevent chemical contamination of the CMT by species in the substrate. Suitable buffer layers include cadmium telluride and zinc telluride. There may be a single buffer layer,

20 e.g. a single layer of zinc telluride or a combination of layers, for instance a layer of zinc telluride may be grown on the substrate with a layer of cadmium telluride grown on top. Cadmium zinc telluride may also be used as a buffer layer.

To grow zinc telluride either zinc telluride may be used as the MBE source

25 material or elemental zinc and tellurium may be used, or a combination of the elemental and compound materials. Similarly the cadmium telluride may be grown using elemental cadmium and tellurium or cadmium telluride or a combination. The buffer layers are grown using standard MBE growth processes which the skilled person will be aware of.

30 After the MBE growth of the buffer layers CMT may be grown on the buffer layers by MOVPE. However it may be preferable to clean the surface of the buffer layers prior to MOVPE growth. Depending on the equipment used it may be

necessary to transfer the buffered substrate from an MBE growth apparatus to an MOVPE reactor and/or there may be a delay between processing steps. If the buffered substrate is not kept in a controlled environment there may be impurities which build up on the surface of the top buffer layer. Cleaning will remove at least some of these impurities. Cleaning may be performed by etching the buffered substrate as is well understood by one skilled in the art of MOVPE or by any suitable cleaning processes. If a combined MBE/MOVPE system complete with load lock between the two parts is in place cleaning is not needed.

10 Prior to growing the at least one CMT layer the method may further comprise the step of growing at least one further buffer layer by MOVPE. This MOVPE buffer layer may be the same as or different to a buffer layer material grown by MBE. As mentioned above MBE gives a good controllable way of growing suitable buffer layers on silicon with the correct orientation for MOVPE growth. In order to further improve conditions for MOVPE growth of CMT however it may be useful to lay down a buffer layer by MOVPE. For instance when the MBE buffer layer comprises a top layer of cadmium telluride grown on a base layer zinc telluride on the substrate the method may comprise the step of growing a further cadmium telluride layer by MOVPE on top of the MBE CdTe layer.

20 Growing a further buffer layer by MOVPE can increase the buffer layer thickness which can be beneficial in some embodiments and MOVPE is a faster growth method than MBE. The MOVPE buffer layers can improve the crystal quality. Further MOVPE buffer layers are also useful in isolating the CMT from the surface which has been exposed to the atmosphere, i.e. laying down an MOVPE buffer layer can cover over any slight surface impurities due to oxidation etc of the MBE buffer layer and any residue of the cleaning process, if performed.

30 Growth of the CMT layer is by standard MOVPE techniques whereby the concentration of the precursors entering the reactor are controlled by their vapour pressure and the gas flow (conveniently hydrogen) through the bubblers containing the precursors possibly with further dilution by an additional clean gas ( $H_2$ ) flow. In this way  $Hg_{1-x}Cd_xTe$  can be grown with a controlled value of  $x$  so as

to give desired device characteristics. Conveniently the MOVPE process uses the interdiffused multi-layer process of CMT growth as described in US4,566,918, i.e. the step of growing CMT comprises sequentially growing thin layers of CdTe and HgTe which interdiffuse during growth to give a single layer of CMT, the relative thicknesses of the CdTe and HgTe layers determining the cadmium content  $x$ .

The organometallic precursors used are any suitable volatile tellurium and cadmium compounds such as an alkyl of cadmium and of tellurium. In one embodiment the tellurium precursor is di-*iso*-propyltelluride and the cadmium precursor is dimethylcadmium.

The CMT layer may be doped with a suitable dopant which may be n-type or p-type. Suitable dopants include iodine, arsenic, indium and antimony although other dopants could be used. Suitable precursors include *iso*-butyllodide and *tris*(dimethylamino)arsenic.

Generally the method will comprise growing more than one layer of CMT according to the requirements of the intended device. Different layers may have different thicknesses, compositions ( $x$  in  $Hg_{1-x}Cd_xTe$ ), and/or different dopants and dopant concentration.

The present invention as mentioned therefore provides a reproducible and effective method of growing controlled cadmium mercury telluride layers which can be used in the production of a wide range of infrared devices. The fabricated layers can be mesa etched, ion beam milled or ion implanted to form devices as is known in the art. The method may include growing one or more capping or contacting layers by MOVPE prior to device formation as would be understood by one skilled in the art. Capping layers may be required if this technique was used for ion milled or ion implanted devices without mesa formation.

Where mesa devices are formed it is preferable that the devices are coated with a passivation layer as will be understood by one skilled in the art. The side walls

of the mesa are preferably coated with one or more passivating layers to ensure electrical stability of the device and prevent loss of mercury from the material. Preferably therefore the method includes the step, after device processing, of coating the devices with at least one passivating layer. The passivating layer  
5 may conveniently be a layer of cadmium telluride. Conveniently the passivating layer is an epitaxial layer grown by MOVPE.

For the purposes of this specification the term device processing may include any steps applied to the CMT material after the initial CMT growth, i.e. any  
10 interruption to the step of growing CMT by MOVPE, in particular steps such as etching which leave a non-planar CMT surface.

The use of MOVPE for growing passivation layers is another novel aspect of the invention. Conventional passivation layers are evaporated layers applied for  
15 instance by MBE or more usually in an evaporator.

The use of MOVPE for device passivation can be advantageous in several regards. First dry etching of mesa devices can result in devices with steep side walls and MBE techniques can increasingly fail to cover the side walls because  
20 the beams of material are parallel to the side walls rather than perpendicular. The MOVPE process, based on gases which are easily able to penetrate the channels between the mesas, is much better at coating such devices.

Further passivation layers such as cadmium telluride grown by MOVPE are  
25 epitaxial with the CMT layers and crystalline, whereas MBE and evaporated CdTe is poly-crystalline.

In fact the ability to grow further epitaxial layers after device processing is a further novel aspect of the invention. This allows for the growth of further CMT  
30 layers after device processing. Therefore the method may advantageously comprise the step, after device processing, of growing further epitaxial layers of CMT by MOVPE. The present method therefore allows CMT samples to be removed from the MOVPE-reactor, put through device processing stages,

replaced into the MOVPE reactor and have further CMT layers grown thereon. Depending on the processing and handling of the samples cleaning may be required after the device processing stages.

- 5 The fabricated devices can then have contacts provided and bonded to a read-out circuit. Where silicon is used as a substrate this results in a device having a thermally matched and IR transparent substrate without the need for thinning processes. Furthermore the present invention provides a means for producing infrared devices on a silicon substrate that work at long wave ( $>8\ \mu\text{m}$ ) infrared wavelengths.

The devices enabled by the present invention include Short wave detectors and sources, Medium wave detectors and sources, Long wave detectors and sources and Very longwave detectors and sources. Dual band, Multi-band, hyperspectral and avalanche devices can be produced using CMT grown by the present invention. Negative luminescence devices can be fabricated as can LEDs and single photon sources and the devices can be used in a range of technology from focal plane array infrared detectors to gas sensors. Transistors can also be fabricated using the method of the present invention.

20 It will be apparent that the invention involves use of two distinct processes, MBE for production of the buffer layers on the substrate, and MOVPE for growth of any additional buffer layers, CMT layers and passivating layers. These two processes may be performed in different pieces of apparatus at different times although as mentioned a buffered substrate not kept in a protected environment prior to MOVPE may need cleaning.

Therefore in a second aspect of the invention there is provided a method of producing a buffered substrate suitable for growth of at least one layer of cadmium mercury telluride by metal organic vapour phase epitaxy the method comprising the steps of taking a crystalline substrate and growing at least one buffer layer by molecular beam epitaxy. The second aspect of the invention

therefore provides a suitable buffered substrate that can be used in the controlled growth of CMT by MOVPE. All of the embodiments of the first aspect of the invention with respect to the growing of the MBE buffer layers are applicable to the second aspect of the invention. In particular, preferably the substrate is mis-aligned from the {100} form towards  $\langle 111 \rangle$  or  $\langle 110 \rangle$ . Preferably the substrate is silicon and the orientation is preferably (001) mis-aligned from  $1^\circ$  to  $10^\circ$  to  $\langle 111 \rangle$ .

In a third aspect of the invention there is provided a method of manufacture of cadmium mercury telluride comprising the steps of taking a buffered substrate comprising one or more buffer layers grown on a crystalline substrate by molecular beam epitaxy and growing at least one layer of cadmium mercury telluride by metal organic vapour phase epitaxy. Thus the third aspect of the invention takes a buffered substrate, such as may be produced by a first aspect of the invention, and grows at least one layer of CMT as required for a particular device. All the embodiments described above with respect to the first aspect of the invention concerning growth of the CMT layers, possible cleaning of the buffered substrate and possible growth of further buffer layers by MOVPE are applicable to the third aspect of the invention.

Because the present invention enables production of CMT for use in infrared devices, e.g. detectors or sources, across the whole range of infrared wavelengths and also enables use of previously difficult substrate materials the present invention allows novel devices to be produced.

Therefore in a further aspect of the invention there is provided an infrared device comprising a substrate, at least one buffer layer on the substrate and at least one layer of cadmium mercury telluride on the at least one buffer layer wherein the substrate orientation is {100} mis-aligned by  $1^\circ$  -  $10^\circ$  inclusive to  $\langle 110 \rangle$  or  $\langle 111 \rangle$ . In this context the term device refers to a material arrangement which is capable of being used as an infrared device when connected to suitable circuitry, for example a detector element in a focal plane array - i.e. it would function as a detector element when formed with appropriate contacts etc. The novel device of the present invention is preferably produced by the method of the present



invention and so all of the advantages and embodiments of the methods mentioned above are applicable. In particular the substrate may be silicon and have an orientation (001) mis-aligned by  $1^\circ$  -  $10^\circ$  inclusive to [111] and the at least one buffer layer may comprise one or more layer chosen from zinc telluride, cadmium telluride and cadmium zinc telluride.

In another aspect of the invention there is provided an infrared device comprising a substrate, at least one buffer layer formed on the substrate and at least one layer of cadmium mercury telluride formed on the at least one buffer layer wherein the at least one layer of cadmium mercury telluride is tuned to be active at long wave infrared wavelength radiation and wherein the substrate is silicon. As used above the term active shall be taken to mean that the CMT is tuned to either detect or to emit long wavelength infrared radiation. As mentioned above fabrication of an array of working long wavelength infrared CMT detectors on silicon has previously not been possible. In the context of this specification the term long wave infrared shall be taken to mean a cut off wavelength of greater than  $8\mu\text{m}$ . The present invention has also allowed production of long wavelength infrared luminescent sources on silicon with excellent performance.

As mentioned above the epitaxial growth of further CMT layers on CMT after device processing is another novel aspect of the invention. Therefore in another aspect of the invention there is provided a method of growing at least one crystalline layer of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  where  $0 \leq x \leq 1$  comprising the step of taking a substrate having at least one mesa device formed in at least one layer of cadmium mercury telluride and growing said at least one layer of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  by MOVPE.

The invention will now be described by way of example only with reference to the following drawings of which;

Figure 1 shows a typical infrared detector arrangement according to the present invention,

Figure 2 shows a generic MBE apparatus that illustrates the principles of MBE,

Figure 3 shows a generic MOVPE apparatus that illustrates the principles of MOVPE,

Figure 4 shows a resistance-area and current-voltage plot at 80K for a device as shown in figure 1 fabricated using the method of the present invention,

Figure 5 shows a plot of  $R_0A$  as a function of temperature for two diodes at opposite sides of a 128x128 array fabricated using the method of the present invention, and

Figure 6 shows an infrared image from a 128 x 128 long wave CMT array on silicon

Referring to figure 1 a typical infrared diode fabricated according to the method of the present invention is shown. The device comprises a silicon substrate 102 having two buffer layers 104, 106. Buffer layer 104 is a thin layer of zinc telluride and buffer layer 106 a thicker layer of cadmium telluride although other buffer layers could be used as will be described.

The device then has three different CMT layers 108, 110, 112. CMT layer 108 is a  $p^+$  doped contact layer. Layer 110 is an  $n^-$  doped absorbing layer and uppermost CMT layer 112 is an  $n^+$  contact layer. Formed on uppermost CMT layer 112 is a metal contact 114 and an indium bump 116 for bump bonding to some read out circuitry. A passivation layer of cadmium telluride 118 is provided over the area of the top CMT layer 112 which is not covered by the metal contact

114. The device therefore exhibits an n-on-p diode structure as will be understood by one skilled in the art. Alternatively a p-on-n structure could be produced by simply reversing the order of layers 108, 110 and 112.

- 5 The device shown in figure 1 may be fabricated using the novel method of the present invention as will be described. First a silicon wafer of the required size is taken and prepared. Silicon is a preferred substrate material as it is transparent to infrared radiation, available in large wafers, of high thermal conductivity, robust and, being silicon, is thermally matched to the read-out circuit. Hence the use of
- 10 silicon substrate eliminates stresses caused by thermal mis-match when the devices are cooled to the operating temperature (e.g. around 80K). However other substrate materials could be used such as cadmium telluride, zinc telluride, cadmium zinc telluride, cadmium zinc selenide, CdSeTe, CdZnSeTe and similar, gallium arsenide, germanium, indium antimonide, indium aluminium antimonide,
- 15 Indium gallium antimonide, indium phosphide, sapphire, alumina or spinel.

The silicon wafer is cut so that the orientation is (001) mis-aligned by  $1^\circ$  to  $10^\circ$  towards [111]. CMT grown on buffer layers on silicon at the {100} orientation has a tendency to form domains and hillock defects. However the present inventors

20 have found that a mis-orientation from (001) of a few degrees towards [111] can eliminate the domains and therefore reduce defects.

The silicon substrate is then etched in hydrofluoric acid/ethanol to leave a hydrogen terminated surface and blown dry with inert gas. Etching may also be

25 carried out using the REOX process. The substrate is then ready to be loaded into the MBE chamber.

MBE is a process which takes place in ultra high vacuum. Referring to figure 2, the liquid nitrogen 202 shroud assists with maintaining the vacuum. The source

30 materials are contained in crucibles inside effusion cells (204) within the machine. The effusion cells (204) are positioned so that the open ends of the crucibles point at a heated substrate (206). Material is transferred from the crucible to the heated substrate when a shutter (208) over the end of the crucible is removed.

The amount of material which is transferred to the substrate is dependent upon the temperature of the crucible, the higher the temperature the higher the vapour pressure of the material and hence the more material is transferred. The heating coils 210 control heating of the crucibles. Because the system is under vacuum, even low vapour pressure materials evaporate if heated sufficiently and can be transferred to the substrate. Again because the system is under vacuum, beams of material are transferred from the effusion cells to the sample without interference from ambient gas. The effusion cells are normally held at an idling temperature where they are kept warm but not hot enough to evaporate material. Before growth is started the cells are warmed to their growth temperature so that sufficient material can evaporate from the crucible to grow the desired layer.

The etched silicon substrates 206 are loaded into the MBE kit via a load lock. The substrate is clipped onto a holder 212 which is heated and also rotates. Rotation assists with the uniformity of the grown layers. The temperature of the substrate during growth is below that at which the deposited material re-evaporates, but is sufficiently hot to allow the atoms to move around on the surface and form crystalline material.

The etched substrate is cleaned at temperature under an arsenic flux. The arsenic flux is initiated by removing the shutter from the front of the arsenic cell and terminated by replacing the shutter. The temperature is lowered to the growth temperature and zinc telluride growth initiated by removing the shutters from in front of the zinc telluride, zinc and tellurium cells as necessary depending on which sources are to be used for the growth. Once the required thickness of zinc telluride has been grown, the shutters are replaced. Likewise the cadmium telluride is grown by removing the shutters from in front of the cadmium telluride, cadmium and tellurium cells as necessary. Again at the end of CdTe growth the shutters are replaced. Once growth is completed, the cells are cooled to the idle temperature and the substrate is cooled and unloaded from the machine.

A thin buffer layer of ZnTe is grown on the silicon substrate by MBE to set the substrate orientation to (001) and to improve adhesion of the CdTe buffer layer

which is then subsequently grown. CdTe grown directly on silicon by MBE is more prone to flaking from the substrate. However for some substrates adhesion is not a problem and a single or base layer of CdTe could be used (e.g. on GaAs substrates). Also for some devices a single layer of ZnTe suffices without an additional CdTe layer. The buffer layers preferably have a total thickness of around 8µm as crystal quality can increase with thickness to about 8µm. However MBE is a relatively slow process and so a thickness less than 8µm may be acceptable.

10 Part of the growth process may be carried out using migration enhanced epitaxy (MEE) and for the purposes of this specification references to MBE include references to MEE.

The CdTe/ZnTe/Si is then transferred to the MOVPE reactor with any etching/cleaning steps as necessary being performed. To produce the device shown in figure 1 three CMT layers are grown, each layer being grown by the interdiffused multi-layer process described in US patent 4,566,918. Whilst MBE apparatus and MOVPE apparatus are often separate pieces of equipment there is no reason why they could not be combined in a single unit with a load lock or transfer mechanism between the two. a particular piece of kit could not be arranged with MBE and MOVPE chambers and a load lock or transfer mechanism between the two.

Figure 3 illustrates the principles of MOVPE growth and shows an apparatus suitable for MOVPE growth although the actual apparatus used may vary. As described more fully in US4,566,918 a supply of hydrogen is supplied via mass flow controllers 3, 4 and 23 from manifold 1 to bubblers 6, 7 and 25. With valve 8 closed and valves 10 and 11 open gas flows through bubbler 6 whereas with valves 10 and 11 closed and valve 8 open the hydrogen flow from mass flow controller 2 is directed via bypass line 14 to a scrubber or filter 31. Similarly bubbler 7 can be controlled by valves 9, 12 and 13 and bubbler 25 controlled by valves 26, 27 and 28. Only three bubblers are shown in Figure 3 for simplicity although more bubblers may be needed in practice. Thus the flow through each

17

bubbler can be controlled. The flow from bubblers 6, 7 and 25 may be mixed in mixer 15 where it may be diluted with gas flow from controller 5 (controlled by valves 32, 33) before entering reactor vessel 16 although in other arrangements it may be preferred to supply the precursors separately to the reactor vessel and  
5 mix them in the reactor.

The buffered substrate 20 is located in the reactor vessel 16 on susceptor 21. A bath of elemental mercury 19 is heated by heating element 17 via reactor wall 24 or any suitable heating means, such as internal cartridge heaters located under  
10 the mercury bath, and maintains a partial pressure of mercury vapour. The buffered substrate is heated by induction heater 18 or heated by any other suitable means so that the metal-organic precursors in the gas streams from the bubblers 6, 7 and 25 decompose in the vicinity of the substrate.

15 Bubbler 6 contains a precursor of cadmium such as dimethylcadmium and bubbler 7 contains a precursor of tellurium such as di-*iso*-propyltelluride. The gas flow from bubblers 6 and 7 to the reactor chamber is controlled sequentially by appropriate control of the valves to grow thin layers of mercury telluride and cadmium telluride, the thickness of the layers being controlled to control the  
20 overall cadmium content of the final CMT layer which is formed by interdiffusion of the layers during the growth process.

To produce the first  $p^+$  CMT layer a p-type dopant should be introduced. A suitable p-type dopant is arsenic although other dopants could be considered  
25 such as phosphorus and antimony. Therefore the dopant bubbler 25 contains a suitable precursor such as *tris*(dimethyl)aminoarsenic (other volatile arsenic components could be used) and the bubbler temperature and gas flow through this bubbler is controlled to give the appropriate doping. After the first CMT layer has been grown the other CMT layers can be grown in sequence. A suitable n-  
30 type dopant for the n-type layers is iodine with say *iso*-butyliodide as the precursor although other precursors could be used and indeed other dopants such as indium could be used. As mentioned where different dopants are used the MOVPE apparatus would have a plurality of dopant bubblers which could be

separately controlled rather than the single dopant bubbler shown in figure 3. Similarly if any MOVPE buffer layers are to be grown the apparatus may contain bubblers holding precursors for the buffer layer constituents.

- 5 Following growth of the CMT layers by MOVPE it is preferable to anneal the material in a mercury rich environment – this fills the mercury vacancies and ensures the desired electrical properties. The annealing may be carried out in a MOVPE reactor and may be performed directly after growth of the CMT layers or it may be performed later using any suitable apparatus.

10

Some two-dimensional arrays of 128x128 detectors on a 55µm pitch were fabricated from CMT material grown as described above and tuned to long wave infrared wavelength operation. Individual diodes were formed by wet etching mesas using hydrobromic acid. A thin crystalline CdTe passivation layer was  
15 deposited by MOVPE.

- Dry etching can also be used; dry etched mesas have much deeper and narrower trenches between the mesas and the use of the gas phase MOVPE process is a considerable advantage in passivation as the gas can more easily penetrate the  
20 narrow trenches. The use of MOVPE for growth of the passivation layer also results in a more robust crystalline CdTe layer unlike the polycrystalline layers formed using conventional MBE passivation layers. Windows were etched in the passivation before metal contact and indium bump deposition – figure 1 refers. One array was flip chip bonded to a silicon leadout chip to measure device  
25 characteristics and another to a readout chip to realise an imaging array of detectors.

- The cadmium composition (x in  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ ) of the absorbing layer was set to correspond to a 10.2µm cut-off wavelength where cut off is defined as 50% of the  
30 maximum response. The diode characteristics were measured as a function of temperature in a cryostat with effectively zero field of view (FOV). The 80K current-voltage (I-V) and resistance-area product (R.A) of one of the diodes in the array is shown in figure 3. The R.A at zero voltage  $R_0A$  and  $R_{\text{max}}A$  are high for a

19

device with this cut-off wavelength ( $\sim 10^3 \text{ Ohm-cm}^2$  and  $\sim 10^4 \text{ Ohm-cm}^2$  respectively). The breakdown characteristics are also excellent, with the R.A value above  $10^2 \text{ Ohm-cm}^2$  at 1V reverse bias.

- 5 A plot of  $R_0A$  as a function of temperature for two diodes located at opposite ends of the array is shown in Fig 4. The expected diffusion and generation-recombination (G-R) limited  $R_0A$  curves for these devices are also shown. The  $R_0A$  values from both diodes are similar for temperatures down to 60K indicating that the CMT composition, doping profiles, passivation and fabrication are
- 10 uniform across the array.

The image from the array bonded to the readout circuit (figure 6) is comprised of 99.7% working detectors. This is the highest reported operability for a long wave CMT array grown on a silicon substrate.

15

- Although in the example given above there was only one growth step of CMT by MOVPE followed by device processing and then MOVPE growth of a passivation layer this later growth step could include growth of further epitaxial, crystalline CMT layers. This allows the formation of complex devices and structures that
- 20 were previously unachievable. The further CMT layers could then be subjected to further device processing steps as required with further re-growth of CMT or passivation layers.



Claims

1. A method of growing cadmium mercury telluride,  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  where  $x$  is  $0 \leq x \leq 1$ , comprising the steps of;  
5  
a) taking a crystalline substrate,  
b) growing at least one buffer layer on said substrate by molecular beam epitaxy, and  
10  
c) growing at least one layer of cadmium mercury telluride on said at least one buffer layer by metal-organic vapour phase epitaxy.
2. A method as claimed in claim 1 wherein the substrate is chosen from the  
15  
group consisting of cadmium telluride, zinc telluride, cadmium zinc telluride, gallium arsenide, silicon, germanium, indium antimonide, indium aluminium antimonide, indium gallium antimonide, indium phosphide, sapphire, cadmium zinc selenide, cadmium zinc selenide telluride, alumina or spinel.
- 20  
3. A method as claimed in claim 2 wherein the substrate is silicon.
4. A method as claimed in any preceding claim wherein the step of taking a  
25  
crystalline substrate includes arranging said substrate to be mis-aligned from the form {100} in either the  $\langle 111 \rangle$  or  $\langle 110 \rangle$  directions.
5. A method as claimed in claim 4 wherein the degree of mis-alignment of the substrate is between  $1^\circ$  and  $10^\circ$ .
- 30  
6. A method as claimed in any preceding claim wherein the substrate is silicon and wherein said silicon substrate orientation is (001) mis-aligned towards the [111] direction

7. A method as claimed in any previous claim wherein the step of growing at least one buffer layer by molecular beam epitaxy comprises the step of growing one or more layers chosen from zinc telluride, cadmium telluride and cadmium zinc telluride.
8. A method as claimed in any preceding claim wherein the step of growing at least one buffer layer by molecular beam epitaxy comprises the step of growing a layer of zinc telluride on the substrate and growing a layer of cadmium telluride on said zinc telluride layer.
9. A method as claimed in any preceding claim further comprising the step, prior to the step of growing the at least one layer of cadmium mercury telluride, of cleaning the surface of the uppermost buffer layer grown by molecular beam epitaxy.
10. A method as claimed in any preceding claims wherein the method further comprises the step, after growing at least one buffer layer by molecular beam epitaxy, of growing at least one buffer layer by metal organic vapour phase epitaxy.
11. A method as claimed in claim 10 wherein at least one buffer layer grown by metal organic vapour phase epitaxy step is the same as a buffer layer grown by molecular beam epitaxy.
12. A method as claimed in claim 11 wherein the step of growing at least one buffer layer by molecular beam epitaxy comprises growing a top layer of cadmium telluride on a base layer zinc telluride on the substrate the step of growing at least one further buffer layer comprises growing a further cadmium telluride layer by metal organic vapour phase epitaxy.
13. A method as claimed in any preceding claim wherein the step of growing the at least one cadmium mercury telluride layer comprises sequentially

growing thin layers of CdTe and HgTe which interdiffuse during growth to give a single layer of CMT, the relative thicknesses of the CdTe and HgTe layers determining the cadmium content x.

- 5 14. A method as claimed in any preceding claim wherein di-*iso*-propyltelluride is the tellurium precursor and dimethylcadmium is the cadmium precursor in the step of growing the at least one cadmium mercury telluride layer by MOVPE.
- 10 15. A method as claimed in any preceding claim wherein the step of growing the at least one cadmium mercury telluride layer involves doping at least one of the cadmium mercury telluride layers with a dopant.
- 15 16. A method according to claim 15 wherein the dopant is chosen from iodine, arsenic, indium, phosphorous and antimony.
- 20 17. A method according to any preceding claim wherein the step of growing at least one cadmium mercury telluride layer comprises the step of growing a plurality of layers of cadmium mercury telluride, at least some of the layers having a different thickness, composition, dopant and/or dopant concentration.
- 25 18. A method according to any preceding claim wherein the method further comprises the step of device processing.
19. A method according to claim 18 wherein the method comprises the step, after the device processing step, of coating the devices with at least one passivating layer.
- 30 20. A method according to claim 19 wherein the at least one passivating layer comprises cadmium telluride.

23

21. A method according to claim 19 or claim 20 wherein the step of coating the device with a passivating layer comprises growing at least one epitaxial layer grown by metal organic vapour phase epitaxy.
- 5 22. A method according to claim 18 wherein the method involves the step, after the device processing step, of growing further epitaxial layers of cadmium mercury telluride by metal organic vapour phase epitaxy.
- 10 23. A method producing a buffered substrate suitable for growth of at least one layer of cadmium mercury telluride by metal organic vapour phase epitaxy the method comprising the steps of taking a crystalline substrate and growing at least one buffer layer by molecular beam epitaxy.
- 15 24. A method as claimed in claim 23 wherein the substrate is mis-aligned from the {100} form towards  $\langle 111 \rangle$  or  $\langle 110 \rangle$ .
25. A method as claimed in claim 23 or claim 24 wherein the substrate is silicon.
- 20 26. A method as claimed in claim 25 wherein the orientation of the silicon substrate is (001) mis-aligned from  $1^\circ$  to  $10^\circ$  to [111].
- 25 27. A method of manufacture of cadmium mercury telluride comprising the steps of taking a buffered substrate comprising one or more buffer layers grown on a crystalline substrate by molecular beam epitaxy and growing at least one layer of cadmium mercury telluride by metal organic vapour phase epitaxy.
- 30 28. A method as claimed in claim 27 wherein the buffered substrate is a buffered substrate produced by the method of any of claims 23 to 26.
29. An infrared device comprising a substrate, at least one buffer layer on the substrate and at least one layer of cadmium mercury telluride on the at

least one buffer layer wherein the substrate orientation is {100} mis-aligned by  $1^\circ - 10^\circ$  inclusive to  $\langle 110 \rangle$  or  $\langle 111 \rangle$ .

- 5 30. An infrared device as claimed in claim 29 wherein the substrate is silicon has an orientation (001) mis-aligned by  $1^\circ - 10^\circ$  inclusive to [111].
31. An infrared device as claimed in claim 29 or claim 30 wherein the at least one buffer layer comprises one or more layer chosen from zinc telluride, cadmium telluride and cadmium zinc telluride.
- 10 32. An infrared device comprising a substrate, at least one buffer layer formed on the substrate and at least one layer of cadmium mercury telluride formed on the at least one buffer layer wherein the at least one layer of cadmium mercury telluride is tuned to be active at long wave infrared wavelength radiation and wherein the substrate is silicon.
- 15 33. An infrared device as claimed in any of claims 29 to 32 wherein the device is a detector.
- 20 34. An infrared device as claimed in any of claims 29 to 32 wherein the device is an infrared source.
- 25 35. A method of growing at least one crystalline layer of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  where  $0 \leq x \leq 1$  comprising the step of taking a substrate having at least one mesa device formed in at least one layer of cadmium mercury telluride and growing said at least one layer of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  by metal organic vapour phase epitaxy.

## ABSTRACT

Manufacture of Cadmium Mercury Telluride

5 A method of manufacture of cadmium mercury telluride (CMT) is disclosed. The method involves growing one or more buffer layers on a substrate by molecular beam epitaxy (MBE). Subsequently at least one layer of cadmium mercury telluride,  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  where  $x$  is between 0 and 1 inclusive, is grown by metal organic vapour phase epitaxy (MOVPE). The use of MBE to grow buffer layers  
10 allows a range of substrates to be used for CMT growth. The MBE buffer layers provide the correct orientation for later MOVPE growth of CMT and also prevent chemical contamination of the CMT and attack of the substrate during MOVPE. The method also allows for device processing of the CMT layers to be performed with further MOVPE growth of crystalline CMT layers and/or passivation layers.

15

The invention also relates to new devices formed by the method.

Figure 1 should accompany the abstract.



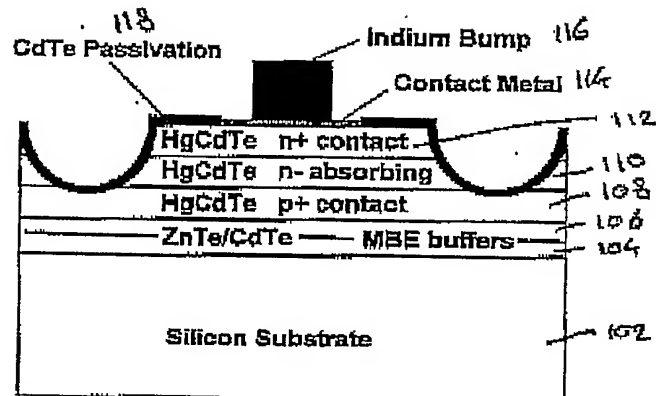
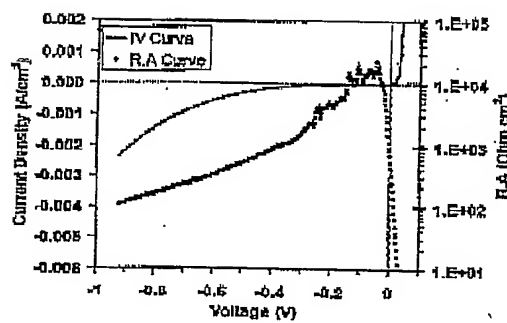


FIG. 1.







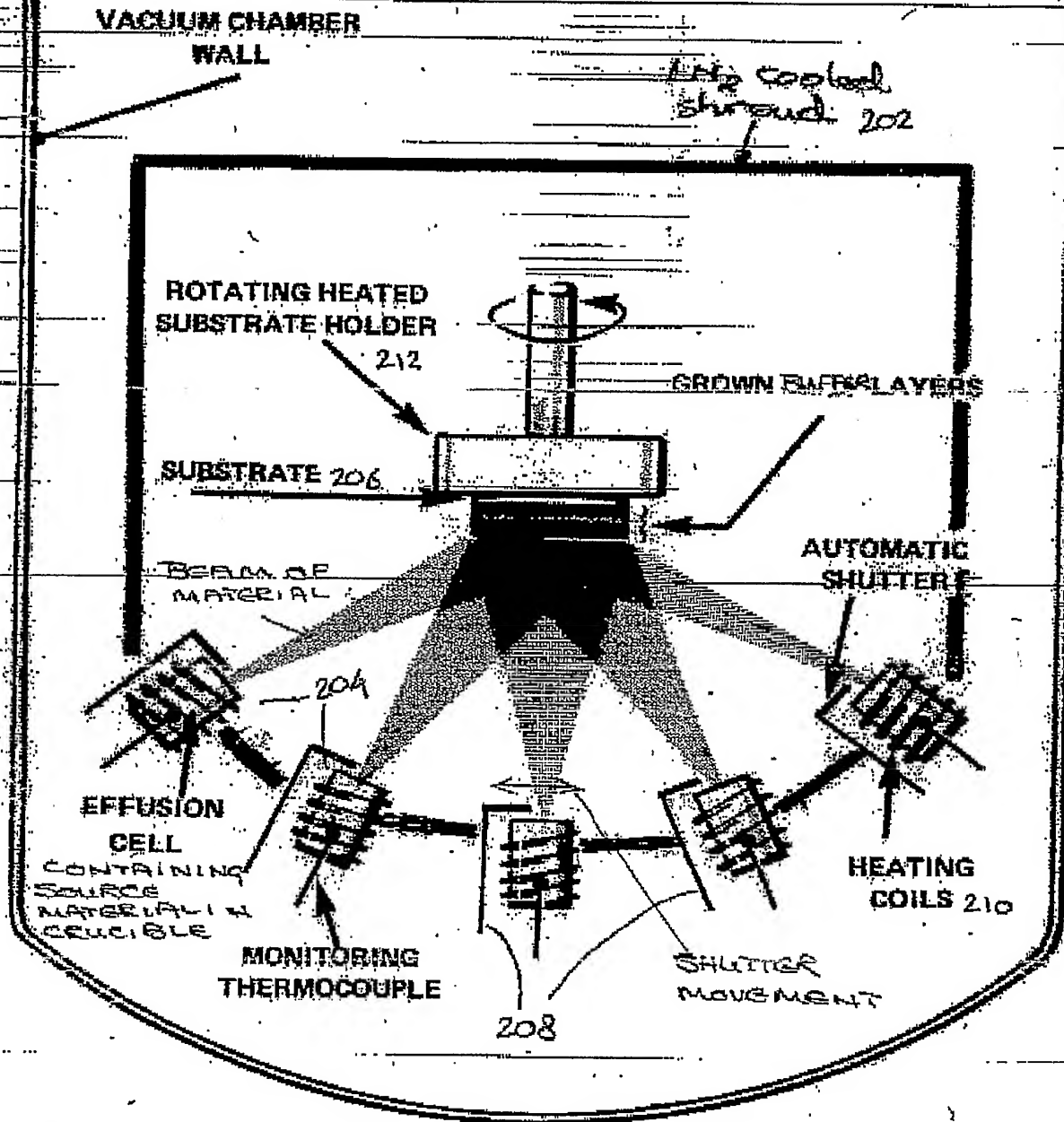


Fig 2

SCHEMATIC OF THE MBE PROCESS

968-94.



3/4

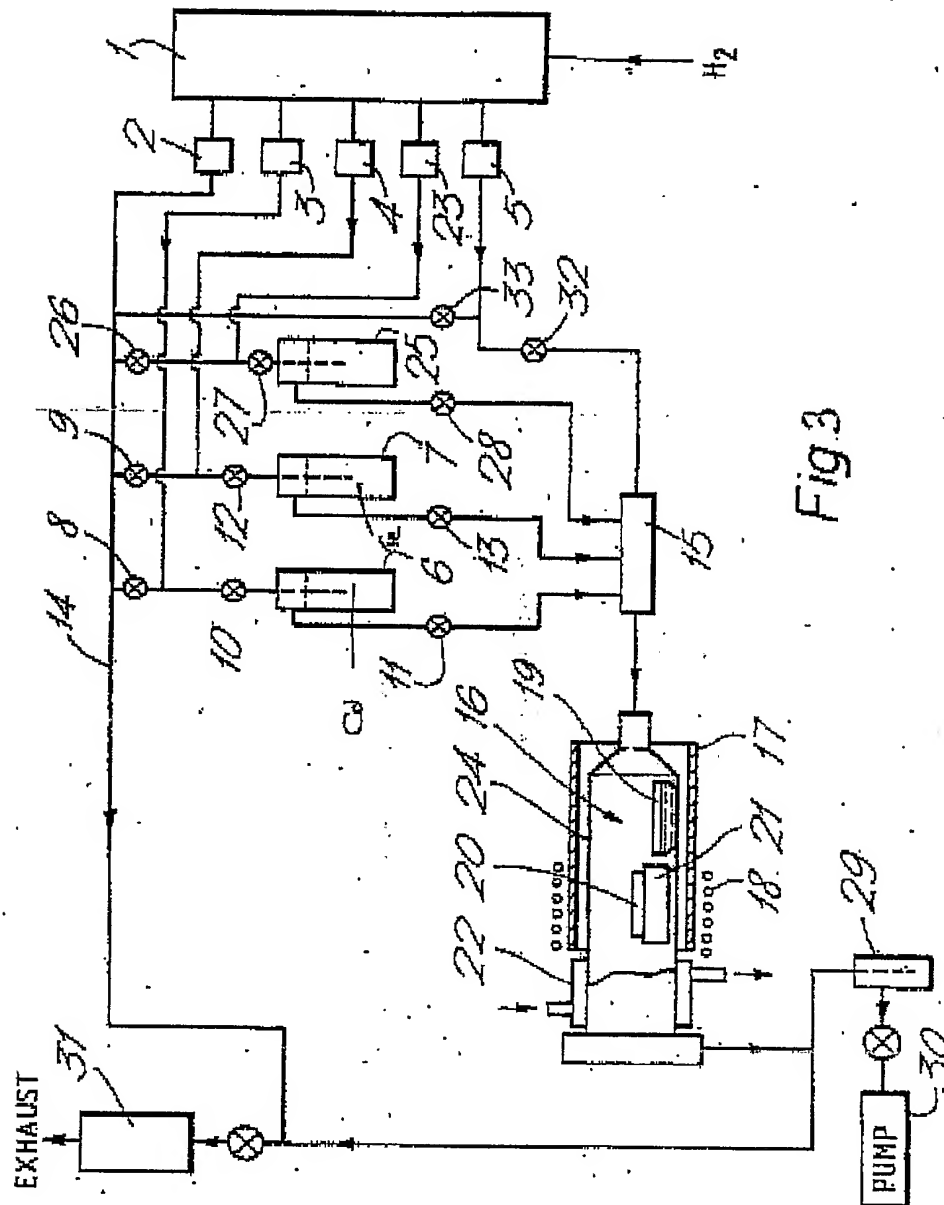


Fig 3



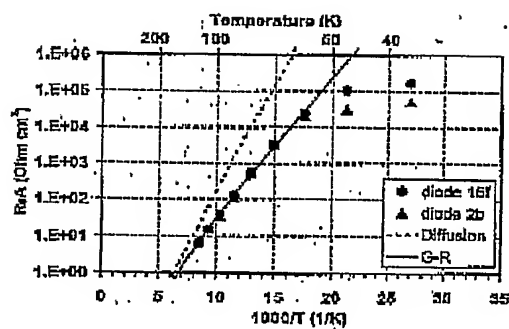


FIG. 5



FIG. 6

